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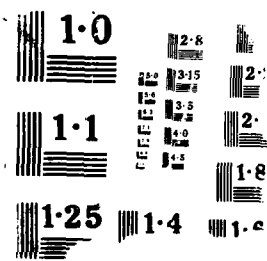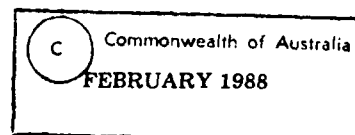
REPORT

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FIRE RETARDANT COATINGS FOR MILITARY
EQUIPMENT - A REVIEW

L.V. Wake

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L.V. Wake

ABSTRACT

A continued increase in the use of fire retardant coatings by the Australian
Defence Forces (ADF) is expected in view of the higher levels of composite and other
lightweight materials being employed in modern military equipment. However, the
increased smoke production reportedly associated with some fire retardant coatings has
led to differences of opinion on the relative benefits associated with their use. This
aspect combined with the growing awareness on health and safety factors associated with
fire has, in part, resulted in a variety of coatings and testing methods being adopted by
allied Service organizations. This review examines the field and discusses the
mechanisms of action and relative performance of fire retardant coatings in relation to
the above. Coatings suitable for use by the ADF are also discussed.

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POSTAL ADDRESS: Director, Materials Research Laboratory
P.O. Box 50, Ascot Vale, Victoria 3032, Australia

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FIRE RETARDANT COATINGS FOR MILITARY EQUIPMENT : A REVIEW

1. GENERAL INTRODUCTION

Fire retardant coatings delay ignition of the substrate by slowing the spread of flames and/or hindering the passage of heat to the substrate. There are a number of different types of coatings which protect the underlying substrate from combustion. Some authors have used the term fire retardant to describe inert coatings which have a high degree of resistance to ignition or decomposition (1), whereas others have suggested that fire retardant coatings are reactively involved in protecting the substrate by forming thermal decomposition products which insulate or protect against the fire (2). Vandersall (3) used the terms nonflammable and insulative to distinguish between these two coating types. Commonly, materials reactively protecting the substrate are further differentiated into intumescent and flame retardant coatings. Intumescent coatings swell to produce a protective insulating barrier between the flame and the substrate while flame retardant coatings react by producing gaseous species on heating which interfere with the flame propagating reactions (4, 5).

It has been suggested (6) that there have been few major developments in flame retardant paints in recent years because of their limited effectiveness. However, the adoption of paints based on chlorinated resins by the US Navy suggests that the flame retardant resins combine good maintenance properties with adequate fire and flame retardancy (see Section 6.4.3). Since the development of intumescent coatings in the late forties and early fifties (7, 8) most attention has been directed towards these materials because of their high insulation efficiency from a limited film thickness. Intumescents are characterised by the ability to rapidly expand to form a stable, inorganic or carbonaceous char when subjected to heat. This is achieved by the production of non-flammable gases which are trapped by the softened film, forming a thick insulating layer which solidifies and protects the substrate. The protective capacity of intumescents, relative to unretarded coatings, was reported by the US atomic weapons test programme (9) as follows: thermal radiation of 12 calories per square centimetre second (cal/cm^2 sec) ignited unpainted wooden structures while those coated with white paint survived 25 cal/cm^2 sec with a blackened wooden surface. Commercial intumescent paints bubbled and expanded at about 12-25 cal/cm^2 sec, and then withstood several hundred cal/cm^2 sec. Since endothermic reactions (sublimation, ablation) can

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only remove a few cal/cm^2 sec, the ability of the refractory char to resist heat transfer is crucially important.

In recent times, considerable attention has also been directed towards high temperature *insulating materials* (10, 11, 12) which slowly erode or ablate with heat. Progress in this area has been greatly assisted by NASA efforts to meet the requirements of higher strength-to weight composites for aerospace. A large number of composite materials have been formulated including the carbon composites used on the wing leading edges and nose of the orbiters (13) which experience temperatures up to 1700°C.

The objective in fire retardant coating research for general military use is for a highly serviceable paint which could be used under sealed conditions, as for example in ship bulkheads and submarines. Such applications demand that the paint evolve no *toxic* vapors during and after painting. Following extensive investigation, Naval Research Laboratories (NRL) in Washington (14) concluded that the evolution of toxic gases in cases of extreme heat or fire is unavoidable in present state-of-the-art fire retardant materials. Furthermore, in many instances the fire retardant additives adversely affected working properties such as appearance, durability, gloss, organic content and flexibility of the paints under investigation.

In severe fire conditions, fire retardant paints would be of little or no significance in preventing the conflagration. Only under conditions where combustion may start from an an isolated source, an electrical short circuit or similar circumstance can fire retardant paints play an important role (15). Different coating schemes have therefore been employed with the aim of providing an effective coating against corrosion, while affording the level of fire protection required.

Australian Defence Forces (ADF) requirements for the use of fire retardant coatings cover a range of equipment and substrate materials. Examples include protection of helicopter tail fins, destroyer guided missile machinery space trunks, ammunition packages, bomb casings, fuel tanks and ship coatings. Such fire retardant coatings are distinct from heat retardant coatings as employed on the heat shield and keel areas in F/A-18 aircraft, the latter coatings simply functioning as thermal insulating barriers to protect hydraulic components and sensor equipment from heat damage.

2. COMBUSTION AND FIRE RETARDATION

The burning behaviour of materials, i.e. flammability, flame propagation, heat production and decomposition products, is not only dependent on the chemical composition but also on physical parameters such as volume, surface area and shape as well as characteristics of the ignition source.

When considering the combustion of common materials, it is normal to consider the process as a heterogeneous reaction with atmospheric oxygen, taking place on the surface of the material. Depending on whether the oxygen supply is higher than

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the rate of reaction of oxygen with the material, the reaction is either activation- or diffusion-controlled. However, as polymers frequently decompose into gaseous products which react with oxygen in a homogeneous reaction, they are often divided into two groups. The first group of polymers thermally degrades with heat such that bonds in the main chain are broken resulting in the formation of low molecular weight gases and liquids, for example poly(methyl methacrylate). At high temperatures, polymers of this group leave very small amounts of nonvolatile residues. The second group of polymers shows a tendency for intramolecular rearrangements, cyclization and recombination which ultimately yield carbonised products, for example poly(vinyl chloride). The pyrolysis of these compounds results in the conversion of linear to cross-linked and aromatic nonvolatile products. The thermal stability and yield of carbonised products increases with aromatic content. A simple empirical equation has been proposed relating the yield of these nonvolatile products and the limiting oxygen index (LOI) (16). Hence, higher yields of carbonaceous products are a measure of improved flame retardancy.

Investigations aimed at retarding the combustion of materials are essentially directed at either reducing the rate of heat release or increasing the rate of heat loss from the combustion reaction. The mechanism of this action may be related to chemical influences (characterised by rate constants of reactions) or physical ones (heat and mass transfer parameters).

A number of speculative modes of action have been proposed for fire retardation including:

    (i)   retardation of reactions occurring on the condensed phase interface;

    (ii)   retardation of gas-phase reactions with gaseous combustion inhibitors which interfere with gaseous flaming reactions;

    (iii)   retardation of combustion by endothermic decomposition of retardant or endothermic gaseous reactions;

    (iv)   generation of noncombustible gaseous products which dilute the gaseous reaction species;

    (v)   barrier formation retarding heat supply to the material and/or transport of reactants to the flame zone.

The mode of action of most fire retardants currently used has not been established unambiguously. Therefore the division of retardants according to mechanistic principles can only be tentative and is often based on very general concepts about the role of the flame retardant on the combustion process which has frequently been related to both condensed-phase and gas-phase processes (17).

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3. HISTORY OF FIRE RETARDANT COATINGS

By the 19th century, Gay-Lussac (18) had found that a number of borates and the ammonium salts of sulphuric, phosphoric and hydrochloric acid were effective as fire retardant compounds. The first reference to the use of fire retardants in paint coatings was in a patent (19) to Louis Paimboeuf in 1837 by the addition of lime, potash, alum and common salts to water or oil based paints. The product, it was claimed, would produce a fire retardant paint suitable for protecting buildings against fire.

Antimony compounds (20), first mentioned as fire retardants in 1884, were not combined with halogenated hydrocarbons until 1936 (21), a mixture still widely used today. Borates (22) were proposed for use in fire retardant paints in 1898 and silicates (23) in 1933. All of these materials are generally used in fire retardant paints known as non-intumescents.

In 1948, a patent (24) was issued to the Albi Chemical Corporation for an intumescent paint which expanded on heating to form a fire retardant protection barrier. The original paints contained water soluble inorganic salts and binders unsuitable for exterior exposure. In recent times, higher molecular weight reactants have been incorporated as the carbon source (tripentaerythritol), intumescent (ammonium polyphosphate) and blowing agent (melamine) to minimise water sensitivity. However some of the more common additives used in intumescent paints still exhibit a degree of water sensitivity.

Reviews on aspects of the development of fire retardant coatings have been published by Ware and Westgate (25), Vandersall (3), Lyons (26) and Hindersinn & Witschard (27).

4. FIRE PROTECTION/DESTRUCTION OF MILITARY EQUIPMENT

The development of fire retardant coatings for Defence use has been greatly influenced by incidents involving the fire destruction of military equipment. A number of these events, including those outlined below, have illustrated the limitations of the coating practice in use at the time and provided an impetus for the development of improved fire retardant materials.

4.1 Coating Developments Arising from World War II Fire Destruction

The use of fire retardant coatings on military equipment arose largely from destruction of ships by fire during World War II (28). Prior to the war, the presence of thin coats of paint was not regarded as a fire hazard. However, the US Navy found that steel ships were no guarantee against fire loss due to the practice of repeatedly painting ships' compartments until heavy layers of paint were built up. The accumulated paint

was sufficiently flammable to spread fire from one sealed compartment to another by heat transmitted through the bulkhead. Burning sheets of paint also fell from overhead restricting those trying to control the fires.

As a result of the Pearl Harbour attack, a specification covering fire retardant paints for coating bulkheads and overheads in US Navy surface ships was developed (29). The alkyd paint which was adopted was fire retardant by virtue of high pigment volume and by incorporation of antimony oxide. The requirement for this paint was that when heat was applied to the rear of the panel, blistering and ignition were retarded. The paint was intended to prevent fire spreading from a sealed compartment to those adjoining it.

4.2 Coating Development Arising from US Aircraft Carrier Fires

Over the past 20 years, the US Navy suffered a number of disastrous fires aboard the aircraft carriers USS Forrestal, (1967), USS Enterprise (1969) and USS Nimitz (1981). Fires caused by aviation fuel spilt on the flight deck spread rapidly enveloping weapons lying on the deck or hung under the wings of nearby aircraft. Within 3 minutes weapons began to detonate or launch propulsively. The catastrophic fire aboard USS Forrestal resulted in the deaths of 133 men (30) while the cook-off on USS Nimitz resulted in the immediate deaths of 14 men and resulted in 60 million dollars of damage (31).

These carrier fires gave rise to a requirement for use of a fire retardant coating to protect bombs, rockets and other ordnance. A programme was established to delay the temperature rise and hence the ordnance reaction for a period of 5 minutes and the extent of the reaction to a deflagration (case rupture and burning of the explosive). This was achieved by the use of intumescent coatings based on an epoxy polysulphide coating incorporating borate salts as the intumescent agent (32).

4.3 Coating Review Arising from Fire Destruction in the Falklands Conflict

The fire destruction of equipment in the Falklands conflict caused considerable disquiet because of the apparent vulnerability of equipment to combustion, e.g. 'the loss of HMS Sheffield followed by the losses of the frigates Ardent and Antelope and the destroyer Coventry raised an immediate outcry because of the speed with which they caught fire' and 'the problem of fire-protection does need urgent action' (33).

The types of materials used in many British ships gave cause for concern. It has since been suggested that PVC coatings must be eliminated (34) as should the use of foam rubber. Ventilation systems and cable runs are two suspect areas for future review. Problems which arose from the use of aluminium in superstructures had became apparent at an earlier date following incidents involving USS Worden off Vietnam and USS Belknap in the Mediterranean (33).

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4.4 Fire Retardant Coatings: Different Services - Different Approaches

Difficulties in selecting a fire retardant coating and suitable testing procedures for military equipment might be expected in view of the range of substrate materials, the differing performance requirements involved and the assorted nature of equipment employed throughout the armed forces. Howeve·, at the present time, little agreement or interaction exists between countries, between Services, or testing organizations on the most appropriate coating for protecting a specific item of equipment or a particular substrate against fire. In many ways, the situation is well illustrated by the fire retardant coatings presently adopted for use on the interior of allied naval vessels.

4.4.1 Fire Retardant Coatings for Allied Naval Ships

The Navies of Britain, US, Australia and New Zealand have, to a large degree, adopted different approaches to the choice and testing of fire retardant coatings used on the interior of vessels. As presently understood, the situation is as follows.

(a)   The US Navy has adopted two fire retardant paints for use on the interior of its vessels, one formulated from a water-based vinylidene chloride resin and the other from a solvent-based chlorendic anhydride resin. This selection is presumed to be based on the extremely high limiting oxygen indices (LOI, i.e. the minimum percentage oxygen level that will support combustion), for these resins compared with possible alternative materials such as acrylics. An atmosphere containing 60% oxygen is required for combustion of vinylidene chloride resin compared to 17.3% oxygen for acrylic resin (see Section 8).

(b)   Personnel involved with fire retardant coatings for the Royal Navy are firmly opposed to the use of materials based on chlorine compounds (35). Their view is that the toxic and corrosive gases produced by coatings containing chlorine derivatives are of far more concern than the flammability of the coatings themselves. The acid products are understood to have subsequently caused electronic failures on a UK naval vessel which sustained fire damage. The description (33) of the deaths of the cooks and control room personnel on HMS Sheffield by toxic gas inhalation from vinyl chloride combustion graphically illustrates the problem of smoke generating materials such as PVC coatings (LOI 46).

(c)   New Zealand Naval personnel involved with ship coatings have stated (36) that they intend to replace the 'ABR 19' (37) fire retardant coating where possible with commercially available gloss latex paints as these were found to have superior fire retardant properties to the previously used solvent based paint. They are also considering an alternative system of the gloss latex paints with added alumina trihydrate for improved fire retardant properties.

(d)   The Royal Australian Navy (RAN) uses the ABR 19 approved alkyd paint as fire retardant for its general shipboard use. The flammability and smoke generation of a large number of organic materials used in RAN ships including adhesives, cellular polymers and laminated materials has been investigated by Brown and Dunn (38).

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(e) Discussion of Naval Paint Schemes

The objection to chlorine containing materials by Royal Navy personnel based on in-service experience, viz 'a balance must be found but ..... smoke generating materials such as foam rubber and PVC must be eliminated' (33) is understandable. However, judged on the ability of a material to burn, the chlorine based resins used by the US Navy are the coatings of choice. US Naval personnel (39) have suggested that smoke generation from ship-board fires is unavoidable and given the greatly improved fire retardant performance of the chlorine based coatings, they opt for these resins. For example, the test results showed that brief ignition occurred for 5-6 seconds with the chlorine based fire retardant while the unretarded paint system flashed into a violent ball of flames which extended to the roof of the test chamber (40).

The use of gloss latex paints by the New Zealand Navy eliminates the necessity of carrying flammable solvents on board ship. NZ has reported decreased flammability of this unretarded commercial latex paint compared with ABR 19 alkyd fire retardant paint, a finding supported by preliminary results elsewhere (36).

5. FIRE RETARDANT COATINGS

5.1 Types of Fire Retardant Coatings

Coatings resistant to combustion have been grouped into a number of categories, the major ones being (i) flame retardants (ii) ablatives (iii) glass-like melts and (iv) intumescents.

5.1.1 Flame Retardant Coatings

As discussed above, flame retardant coatings produce gaseous species which inhibit reactions in the flaming process. It is generally agreed that flame retardant paints, although having excellent brush application and flow properties, give far inferior fire protection than intumescent paints. Funt & Magill (41) have shown that fire retardants operating by flame inhibition can be defeated by even moderately elevated temperatures. Consequently, decreasing attention has been directed towards coatings whose action is confined to inhibiting flame propagating reactions except in specialised areas.

5.1.2 Ablative Coatings

Ablative coatings provide excellent fire exposure protection for structural steels. Their function is based on gradual erosion of the coating by energy absorption from a fire. To change the virgin solid coating into a gaseous composite requires heat

input that would otherwise be absorbed by the structure being protected. The temperature rise of the protected structure is retarded in direct proportion to the ablative coating thickness and its thermal properties. With the assistance of NASA support in recent years, high temperature oxidation-resistant polymers such as phenolics, polybenzimidazoles, polyimides, polythiazoles, polyphenoxazines and epoxies (42-45) have been proposed and/or employed in these coatings. Phenolics, for instance, do not burn under ordinary conditions particularly in composite form. Phenolics filled with mica, fibres and minerals have obtained the most recent Underwriters Laboratory classification of SE-0 rating (46).

5.1.3 Inorganic Coatings which form Glass-like Melts

Paints made with alkali silicates or borax form glass-like melts during a fire which form a barrier between the air and the flammable substrate. Steel panels painted with this type of finish can be heated to 900°C. The major problem with these coatings has been that alkali silicates tend to be brittle and water sensitive. Consequently, these earlier forms have been of decreasing importance.

Currell (47) has suggested that the brittleness of the silicates is the result of 0.17 network bonds per unit volume. Silicones (polydimethylsiloxanes) on the other hand have 0.03 bonds per unit volume which gives them excellent flexibility but inferior mechanical and thermal properties. Ray (48, 49) also drew attention to the importance of network connectivity in these glassy materials pointing out, for example, that those with 3-connected building units have a lower Tg (e.g. 270°C) than those with 4-connected building units (e.g. 1200°C). By appropriate selection of inorganics, a suitable coating may be achieved.

In recent times, attention has been directed at overcoming the shortcomings of the inorganic coatings. One of the methods used to improve the mechanical properties of inorganic compositions has been by the incorporation of fibres frequently referred to as bridging agents into the matrix. Recent work has resulted in the complete replacement of the inorganic matrix with inorganic fibres, producing thermally resistant materials that can be heated to 1500°C and dropped into liquid nitrogen without damage (50).

State-of-the-art inorganic coatings include systems filled with intumescent compounds such as hydrated salts, minerals and organic agents. Some of the alkali metal silicates are also reported to be intumescent film forming materials and are used with and without fillers (51). An inorganic intumescent is also available in sheet or paste form (52). Inorganic coatings represent the most obvious way for achieving smokeless fire retardant coatings.

5.1.4 Intumescent Coatings

An intumescent paint is required to expand to form a cellular foam which has good insulating properties and resistance to combustion. A well known example of the phenomenon of intumescence is the popular classroom demonstration of the action of acids on carbohydrates. In this instance, the dehydrating action of concentrated acid on sugar produces a voluminous low-density carbonaceous solid.

It has been suggested that for an intumescent coating to function successfully, the following properties are required (53):

(1)   The binder polymer should soften or decompose below the activation temperature of the intumescent agent,

(2)   The binder should be expanded by the intumescent agent,

(3)   The binder residue should contribute to the stability of the intumesced foam produced by the agent,

(4)   The binder system should be nonburning or self extinguishing when exposed to a flame and preferably endothermic upon anaerobic thermal decomposition.

Intumescent paints have generally been formulated with a carbon source (e.g. a polyol), a blowing agent (e.g. chlorinated paraffins or melamine) and a dehydrating agent (generally an acid precursor such as ammonium polyphosphate). Satisfactory operation of intumescent paints requires that these three chemicals operate at the right time and in the required sequence. For example, decomposition of the blowing agent at too low a temperature will result in the gases escaping before the char can be formed, while decomposition at too high a temperature will destroy the char.

It has been suggested (54) that some variation in activation temperatures of the components of intumescent coatings might be desirable for different requirements. Commercial systems are reported to be available from a NASA supplier which are suggested to operate between 180°C and 600°C. Little published information is available on these coatings.

In recent times, self-intumescent compounds have been developed (55) such as with nitroaniline sulphate and the sulphanilimides (9). The nitroaniline-sulphate compounds unfortunately intumesce exothermically (9, 56) and while the sulphanilimides are free of this defect, their foams were found to have poorer insulating and fire resistant properties than foams formed from the traditional phosphate fire retardant compounds (9).

5.2 Properties of Fire Retardant Paints

One of the most difficult tasks of the formulator is to achieve the desired level of fire inhibition while retaining the functional properties of the coating. Coating thickness requires a balance between fire retardant performance desired and the weight penalty resulting from the thicker coating. As good fire resistance commonly requires high levels (10-20%) of fire retardant, these coatings frequently suffer from poor mechanical properties. Related properties which may also be affected by these high filler levels include:-

application properties,	abrasion resistance,
flexibility,	cleaning properties,
solvent resistance,	hardness,
scrub resistance,	gloss levels,

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shelf life,   exterior durability,
and water sensitivity.

Intumescent coatings which achieve their action by chemical incorporation of
the active agent directly into the binder are presumed to have better coating properties,
e.g. gloss levels than coatings with intumescent fillers.

Certain pigments are known to greatly improve the performance of fire
retardant coatings (9) whereas others are believed to be detrimental.   Vandersall (3) has
suggested that finely divided solids such as pigments may improve the intumescence of
fire retardant coatings by assisting nucleation of the blowing agent. In contrast, Ryles
(5) has suggested that 'most of the pigments commonly used to tint paints seem to have
a deleterious effect on intumescence.   The worst are the organic pigments; if possible,
only metal oxides should be used'.

6.   FIRE RETARDANT COATINGS FOR DEFENCE USE

Protection of equipment generally involves the use of a paint coating applied
to a steel, aluminium, polymer or composite substrate. In recent years, high
performance coatings have been increasingly adopted for military equipment and have
included the thermosetting epoxies and urethanes. A typical high performance scheme
for steel or aluminium involves an inhibited epoxy polyamide priming paint and a
polyurethane topcoat while organic polymer substrates are commonly painted with
polyurethanes. The alkyd paints and nitrocellulose lacquers prevalent in former times
are of decreasing importance. The fire retardation of these coatings is discussed in 6.1-
6.4 below and summarised in Table 1.

Fire ratings on structural steel are given in terms of the length of time a
coating will maintain the temperature of the steel below approximately 540°C (1000°F)
(2). In the case of aluminium, protection below 177°C (350°F) (2) is required and for
many plastics, below 100°C.

6.1 Epoxies

Epoxy resins formulated with amides, amines and polyesters are widely used
for the protection of allied Defence equipment, particularly as priming paints.   US Navy
also uses a fire retardant epoxy-polysulphide to protect explosives, the so-called 'NASA
fire retardant' coating scheme.

Epoxy resins are flammable materials, a property that can be reduced by
using fillers particularly those evolving water vapour, e.g. epoxies (26) filled with 60%
hydrated alumina have an LOI of 40.8 (cf. 19.8 for a nonretardant system).

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Fire retardant epoxy resins may be prepared either by simple addition of fire retardant compounds or by modification of the resins to chemically incorporate these elements. It has been suggested that 5-6% phosphorus is required to attain significant fire retardation (26), although one reference suggests that 2% phosphorus is sufficient if ammonium polyphosphate is employed (57). As with other types of coatings, formulation with both phosphorus and chlorine elements is reported to produce self extinguishing epoxy resins at lower phosphorus levels than by phosphorus alone (58).

A wide variety of phosphorus and halogen-containing compounds have been employed to retard epoxy resins, both by addition and by chemical modification of the resins. Phosphorus-containing compounds used as additives include ammonium phosphates, organophosphorus compounds and phosphorus-halogen mixtures. Phosphorus trianilide (59) has been proposed as an intumescent agent with even better water washability than ammonium polyphosphate. A clear intumescent epoxy coating (60) has been prepared by reacting triphenyl phosphite, which had been known to be a reactive diluent (61) with an epoxy resin. The coating is apparently devoid of the storage instabilities of conventional intumescent systems but is reported not to intumesce when pigmented (62). Chlorine on an aliphatic portion of the resin is preferred to that on an aromatic nucleus for fire retardant activity (63).

Addition of boron compounds including boric oxide (64), borates (65) and organoborate esters (66) are all reported to produce self extinguishing epoxy resin systems (an LOI of 28 is considered self extinguishing). About 20% boric oxide renders an epoxy resin self-extinguishing. Organic esters of boron acids such as trimethoxyboroxine, a borolane or a borinane (67, 68) have been used which dissolve in the resin. General Electric (69) found that triphenylantimony was an effective flame retardant in an epoxy resin and that addition of a halogenated compound did not further affect flammability.

Reports on chars of intumescent epoxy coatings (6, 51) suggest that they tend to be more durable than those formed from a number of other coatings e.g. neoprene. Selection of the intumescent was found to be critical to adhesion of neoprene chars but not to those from epoxy resin systems.

6.2 Polyurethanes

Polyurethane coatings are widely used in Defence applications because of their excellent long term performance, outdoor durability and chemical resistance. Their use is mainly confined to two-package systems comprising isocyanate prepolymers and polyols.

It has been suggested (70) that a survey of the literature does not give much detail of the exact nature of polyurethane flammability. The combustion of the polyurethanes is believed to occur mainly from pyrolytic decomposition of the resin to low molecular weight volatile species which undergo luminous reactions in the flame (71, 72). The soft polymer segment is particularly amenable to this process. Direct oxidation of carbon in the polymer phase, sometimes known as 'punking' or 'afterglow' is not regarded as a great problem with urethanes. Degradation is complex and is obviously dependent on the starting materials. Unzipping to starting materials may occur at lower temperatures. Loss of carbon dioxide results in the formation of olefins

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and primary amines and may be followed by formation of secondary amines (73).

The fire retardant requirements of the polyurethanes are lower than other condensation polymers (4) presumably because they contain a high percentage of nitrogen. It is known that the structure of the polyurethane has a significant effect on flammability. Einhorn et al (74, 75) have studied char formation and smoke generation in a series of polyurethanes with and without fire retardants. For the polyisocyanates, toluene diisocyanate (TDI) gave the poorest flame ratings, the poorest chars - often none - and produced the least smoke. Conversely, the least combustible sample, polymethylene polyarylisocyanates produced the best char and the greatest smoke.

Only a few reports have been directed at the thermal stability of the soft segments connecting the carbamate units in polyurethanes. These are normally polyalkylene ether units or polyesters. Polyester linkages are reported to give better flame ratings than polyethers (76). Of the polyethers, the low molecular weight polyethers give better flame retardation than the high molecular weight polymers (77) presumably as the former require more polyisocyanate for curing.

Trimerisation of isocyanates produced ringed isocyanurate structures with burnthrough times increased by a factor of 10 or more over isocyanates (78). Ring structures in the polyol component were also found to improve fire resistance. The use of trimellitic anhydride with polyetherpolyols decreased the weight loss after fire testing to 16% compared to 85% for other polyols (79). The incorporation of epoxy groups into urethanes was also found to improve the fire retardancy of the systems. This was suggested to occur because of the formation of cyclic polyoxazolidones (80).

6.2.1 Non-Reactive Additives

Most fire retardants have been developed for urethane foam systems. Durability of the treatment for coatings intended for outdoor use is important as is coating performance. In view of the great potential importance of polyurethanes, methods for lowering the flammability are receiving increasing attention. The literature on fire retardant polyurethane coatings has been reviewed by Papa (71), Wen-Hsuan Chang (4), Frisch and Reegan (70) and Lyons (26).

As with a number of other coatings, decreased flammability of polyurethanes can be obtained by incorporating fire retardant additives such as polyhalogenated compounds, antimony oxide and phosphorus compounds into the coating. A wide variety of additives, both nonreactive and reactive have been proposed, however only a small number have shown commercial importance (81).

Lyons (26) suggested that flame retarded polyurethanes (generally foams) often have a tendency to generate excessive smoke, a problem which he believes requires further research. Frisch and Reegan (70) have likewise reported that the addition of phosphorus and/or halogen containing compounds, either in the form of an additive or a reactive component, results in relatively high smoke evolution, limited heat resistance and in many cases, reduced hydrolytic stability.

It has been noted (82) that the incorporation of some fire retardants in polyurethanes, notably phosphorus, tends to render the polymers less thermally stable.

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In the cases studied, the initial decomposition temperature was lowered, but the char yield was increased at higher temperatures (83, 84).

Of the additive fire retardants, antimony oxide is the most often reported, generally in association with chlorinated organic compounds (85).

Phosphates perform very well in urethane systems at relatively low concentration (ca 1.5%), however many of them are water soluble and do not dissolve in the urethane components. Materials containing ammonium polyphosphate, which is less water soluble than the inorganic monophosphates, show excellent retention of fire retardancy after short immersion periods (86). They are reportedly effective (87) at a 4% level (1% P) in passing ASTM 1692 fire resistance. Melamine phosphate has been used (88) instead of the inorganic phosphates to overcome the settling problems which result from the insolubility of the latter in these high performance resins.

Comparatively, it has been reported (89) that the type of phosphorus-containing fire retardant matters little as long as it can decompose to acids on heating. However, Lyons (26) examined phosphates, phosphonates and phosphites and concluded that phosphate was the most effective form of phosphorus as a fire retardant in urethanes. Analysis of residues has revealed no appreciable loss of phosphorus content up to $700^{\circ}C$ (79, 82).

Most of the phosphorus-halogen compositions are additive materials rather than reactive compounds. The benefits of halogens in urethanes seem only marginal for while 1.5% phosphorus is needed to retard polyurethanes in the absence of halogens, the level is lowered to 1% in the presence of 10-15% chlorine (26).

It was noted that polyurethanes were found to have a lowered flammability with halogenated phosphate esters if formulated with certain silicone surfactants, an effect presumed to be physical (90). Another report (91) suggests that ferrocene is both a flame retardant and smoke suppressant. Alumina trihydrate, widely used to reduce flame retardancy of organic materials, was found to be relatively ineffective in polyurethanes by itself, although effective in combination with halogenated compounds (92).

Myers et al (93) found that ammonium pentaborate mixtures gave much better results in a thermoplastic polyurethane than did ammonium polyphosphate.

6.2.2 Reactive Flame Additives

The chemical incorporation of reactive fire retardants into polyurethane resins is considered important where urethanes are employed as topcoats exposed to the weather. Chemical bonding prevents the retardant leaching from the resin during long-term exposure. Some researchers have also reported that chemical incorporation into the resin gave better fire retardancy than simply blending of nonreactive additives, at least for phosphorus (86).

A large number of the reactive compounds are comonomers broadly classified into three basic types: phosphorus-containing polyols, phosphorus- and halogen-containing

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polyols and highly aromatic polyols. They are incorporated into the polyol component by virtue of the fact that synthesis of the polyisocyanates requires complicated technology involving the reaction of phosgene with polyamines.

Phosphate polyols represent the least expensive solution as fire retardants but they exhibit moisture sensitivity. Consequently, they are of limited value in producing durable flame retardant polyurethane coatings. To improve the hydrolytic stability as well as flame retardancy, polymers have been prepared containing the phosphorus directly bonded to carbon. They have been prepared by condensing phosphorus containing diamines with bischloroformates. These polymers were found to have comparable stability to non-phosphorus containing urethanes against alkaline hydrolysis. A film produced from one of these polymers exhibited self-extinguishing properties. A number of such compounds have been incorporated into polyurethane polymers (94-95) but their usefulness in polyurethane coatings has not been established.

In summary, it is difficult to evaluate the overall performance of the various fire retardant systems because of the large number and variety of polyurethane formulations. Information on them comes from patents and product bulletins. Several patents on materials for use in fire retarding polyurethane coatings have appeared (95-105).

6.3 Acrylics

Acrylic polymers are extensively used in coating systems on military equipment, buildings and fixed installations. The two forms of acrylic coating in common use are acrylic latex paints and solvent-based acrylic lacquers. The acrylic latex paints are widely used as interior/exterior decorative paints on constructions and more recently on interior areas of Naval ships from the United States and New Zealand. The acrylic lacquers are used as durable topcoats on certain items of military equipment, e.g. Australian F-111C aircraft.

Acrylics are considered to be highly combustible. Plastic sheets are roughly comparable to wood in flammability and ignition characteristics (106). Latex paints with fillers and pigments are apparently much less flammable and in an examination of a large number of materials by the ASTM E-84 25 ft tunnel test, latex paints were reported to have the lowest flame spread of all materials tested (107). The thermal degradation of acrylics is dependent on the substitution of the carbon atoms of the backbone. With no substitution, little monomer is recovered; with substitution, the polymer unzips such that the product is almost entirely monomer (108). Addition of an acid-forming fire retardant alters the decomposition products of poly(methyl methacrylate) to produce large amounts of carbonised deposit in a manner similar to the retardation of cellulose decomposition (109).

The acrylates are fire retarded principally with phosphorus compounds ranging from phosphates to phosphonium compounds. Self-extinguishing poly(methyl methacrylates) have been produced by adding about 8% phosphoric acid to the monomer and then polymerising to give a polymer containing about 2.5% P (110). Poor flame retardancy was obtained with trimethylphosphine oxide, a volatile species, whereas maximum oxygen index elevation was achieved with phosphoric acid (111).

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Fire retardants effective for acrylate polymers include reactive monomeric additives with polymerisable double bonds for copolymerising into the polymer and additive materials which are either soluble or insoluble in the polymer network. Phosphorus-containing methacrylate and acrylate esters are easily prepared and many compounds have been synthesised. Likewise, examples of halogen-containing esters and halogen/phosphorus containing methacrylate and acrylate esters are also numerous. Phosphorus in these polymerisable forms is mainly in the form of phosphonates with the exception of a hydrophosphite.

Of the additives, the phosphorus-halogen compositions have found favor commercially on a cost effective basis. Many of these compounds serve as plasticisers. The effect of chlorine is to reduce the phosphorus requirement from about 5% to about 2%. This reduces the amount of retardant required from about 40% to around 15% so that gloss levels, and other properties will be less affected. Cass & Raether (112) found that improved results were obtained from a halogen-containing polyphosphonate when compared against three halophosphate esters which they partly attributed to the higher molecular weight of the phosphonate making the compound less of a plasticiser.

6.4 Miscellaneous

6.4.1 Silicones

Silicone coatings may be considered to be heat resistant rather than fire retardant coatings and offer good protection up to $350^{\circ}C$. The addition of heat resistant pigments such as aluminium can raise this to $550^{\circ}C$. They are therefore widely used in high temperature environments such as on aircraft engine and gear components.

6.4.2 Phenolics

The British Navy Ships Materials Committee has reported (113) that 'emphasis is now being placed on the possible use of phenolic resin as fire retardants in structural applications. Although polyester resins are acceptable at present, the potential advantage of phenolics in fire are such that they cannot be ignored'.

6.4.3 Coatings Containing Chlorine Based Resins

(a) Vinylidene chloride/vinyl chloride resins

The US Navy have recently adopted a water based vinylidene chloride fire retardant coating for use on the interior of naval vessels. This paint (formulated to F-25A) has proven to be superior to the traditional fire retardant paint system (40).

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(b) Chlorendic anhydride based resins

Chlorinated alkyds based on chlorendic anhydride have been employed in US Naval vessels for a number of years as the interior fire retardant paint coating. The material was formulated to a given specification (F-124) and tested to Military Specification DOD-E-24607. This paint, which until recently been the interior workhorse for USN vessels, shows good fire retardant properties.

7. CHAR PROPERTIES OF INTUMESCENT PAINTS

The theory of char effectiveness (3, 9, 51) is based on the char yield and its insulation efficiency depending on the cell structure and its reflectance. The rate of heat transfer through the char determines how long the substrate can be protected. Parker and Winkler (114) have shown that the primary thermochemical anaerobic char yield as measured from a thermogravimetric analysis bears a direct relationship to the number of multiply bonded aromatic rings present in the initial polymer. Since the thermal conductivity of gases is approximately an order of magnitude lower than solids, conductivity is best reduced by reducing the density of the foam.

The structure of the char depends on the staging of the blowing agent relative to the formation of a critical viscosity in the semi-molten layers formed by the active filler and the binder system. If the blowing action occurs too early, the intumescent action is reduced because the molten material is too viscous. If the action occurs too late, solidification of the char inhibits intumescence. If the molten material becomes too fluid, i.e. the viscosity becomes very low, large cells are formed during the blowing process and gel in the char. These large cells are relatively ineffective and the char can become quite frangible. However, providing that the char is composed of small tough, closed cell structures, char integrity should be favoured.

The radiative heat transfer through a fire protective coating is controllable either by the reduction of emissivity or by the increase in the reflectance of the coating (char). Systems with low emissivity at a given wavelength have a high reflectance, i.e. $s + e = 1$ (where s and e are reflectance and emissivity (9)). It was found that the oxides which provided the highest reflectance, titanium dioxide, zirconium dioxide, and phosphate and antimonate glasses consequently have very low emissivity. As such, these pigments greatly assist in reducing the radiative heat transfer through a char layer.

The properties of char toughness and durability are of critical importance to the performance of the intumescent. A program (5) in which the individual constituents of an intumescent system were systematically varied revealed adhesion problems with many of the intumescent formulations and unexplained variability in others. The study also showed that intumescent compounds which operated satisfactorily in one binder did not necessarily work in another and that careful selection of the system was necessary.

AWRE in the late 1950's developed an epoxy based system with a very high content of foaming agent. This gave enormous char/virgin expansion ratios of 50:1 or

even 100:1 and correspondingly high performance figures under ideal conditions. However, the resulting light, fluffy char was easily blown away in light winds or convection currents. Since that time the commercial suppliers of this type of product have adopted more conservative ratios of between 4:1 and 8:1 by using less foaming agent (54).

8. EVALUATION OF FIRE RETARDANT PAINTS

A coating must be exposed to a fire or heat source of known intensity in order to establish its fire resistance rating which is determined by the length of time that it successfully performs during exposure. A large number of different tests have appeared over the years to rate the fire retardancy of materials. Recently, the trend has been to adopt the methods which best simulate the end use of the coating.

Many fire tests begin with exposure to a fire source until ignition is achieved. The fire source is then withdrawn and observations continued. This method has been the most common single-point test. However, many materials which show good fire retardant properties at one heat flux may perform poorly at higher values so that tests on isolated materials should cover a range of conditions. Fire retardants operate by increasing the threshold of ignition of materials. The effect of raising the heat flux is that fire retardant polymers will burn when the flux is high enough and for many polymers the retardant effect is removed at high fluxes. It has been suggested that tests for assessing fire retardants vary in effectiveness according to which of three stages of a fire the measurement is associated. These stages are (i) ignition, (ii) flame spread, or (iii) extent of conflagration.

Brief descriptions of the more commonly used fire testing procedures for coatings are given below:

ASTM E 84-70 (25 ft Tunnel) (115)
Monsanto 2-ft Tunnel (116)
ASTM D 1360-70 (Cabinet Flame Test)
British Standard BS 476 (Flame Propagation)
ASTM D 2863-74 (Oxygen Index)
ASTM E 162-67 (Radiant Panel) (117)
ASTM E 136 (Noncombustibility of Elementary Materials) (117)
US Navy's 'Resistance to Ignition Test' (117)
Lockheed 37-676 (Coating Heat and Fire Resistance Test) (118)

ASTM E 84-70 tunnel test (115) was developed by the Underwriters Laboratories of the USA. The test determines flame spread, fuel contribution and smoke development. The test consists of a 25-ft long horizontal flue with the sample to be tested forming part of the tunnel. The sample size is 25-ft x 20-inch. The chamber is sealed and a controlled gas-fed flame impinges on one end of the sample and ignites combustibles present. The flame is applied for 10-minutes and the advance flame front is recorded during the test. The term 'flame spread' is an arbitrary rating based on asbestos-cement board - rating 0 and red oak - rating 100. A flame spread of 25 or less

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is often required for critical areas. (Some consider that the most important factor in saving lives and minimising property loss in a fire is the flame spread which led to the development of this test).

The Monsanto 2-ft tunnel test (116) was found by Monsanto to correlate with the expensive 25-ft tunnel test. The 2-ft tunnel consists of 24 x 4-inch angle iron inclined 28° from the horizontal. A window in the side of the tunnel permits flame spread to be determined. The coated substrate, 23-7/8 x 3-7/8 inch, is placed coated side down over the burner. The coated panel is burned for 5 minutes and the maximum flame spread measured. Insulation value, degree of intumescence, char volume and afterglow can be measured. This test is reported to be an excellent method for evaluating coatings.

ASTM D 1360-70 cabinet flame test is one of the oldest tests for evaluating the flammability of coatings. Height of intumescence, weight loss, char area and volume can be measured but not flame spread. The 8 x 12 inch panels are placed at 45° coating side down in the cabinet over a flame fuelled by 5 ml of absolute ethanol.

ASTM D 2863-74 determines the limiting oxygen index of the film. In this test, a film of the coating is suspended in a vertical position in the chamber. The oxygen level in the chamber is adjusted to permit ignition and then reduced at a specified rate until the flame extinguishes.

The British Standard 476, pt 7 (1971) 'Surface Spread of Flame, Test of Materials' is designed to assess the ability of various paints to influence the spread of flame across their surfaces. This test requires a vertically mounted radiation panel, 900 mm square with a concrete refractory surround. On one side of the radiant panel, a specimen holder is hinged to the surround so that when placed in position, it is flush with the inner face of the surround. A vertical gas flame is applied to one end of the radiant panel for one minute as the specimen is exposed to the radiant panel. The time of flame spread is recorded at 1 1/2 and ten minutes by measuring distances from the bottom edge of the specimen.

US Navy (40, 117) uses the ASTM E 162-67 'Surface Flammability of Materials using a Radiant Heat Energy Source' for evaluating nonflaming coatings. The radiant heat source is a 12 x 18-inch panel in front of which is inclined 6 x 18-inch specimen, the upper edge of which is closer to the source. A pilot burner, capable of being swung out of position when not in use, is mounted horizontally to provide a 2-3 inch flame of gas. The position of the burner tip is such that the flame will be in contact with the top centre area of the sample. Ignition occurs near the upper edge and the flame front progresses downward. A factor derived from the rate of progress of the flame front (ignition properties) and another relating to the rate of heat liberation by the material are combined to provide a flame spread index. Provision is also made for measurement of the smoke evolved during tests.

US Navy (117) is also considering the use of the ASTM E 136 'Noncombustibility of Elementary Materials' for evaluating nonflaming, fire-protective coating compounds. This method is designed to identify the noncombustibility of materials to indicate those which do not aid combustion or add appreciable heat to an ambient fire. In this apparatus, two concentric refractory tubes are arranged with heating coils outside the larger. A controlled flow of air is passed down the outer tube and then up the inner tube. The 1.5 x 1.5 x 2-inch sample is placed in the inner tube

with thermocouples. The temperature is maintained at 750°C. The thermocouples are monitored and materials are reported as noncombustible if the recorded temperatures do not rise 30°C above the furnace air temperature and if there is no flaming of the specimen after the first 30 seconds.

The only widely recognised method used for determining the fire retardancy of coatings for the Australian Navy has been the Australian Standard K179-1969 'Semi-Gloss Enamel - Low Fire Hazard for Noncombustible Surfaces (Primarily for Service Use)' which is based on the UK MOD Defence Specification Method Def-1114, 'Paint Finishing, Fire Retardant, White and Tinted White'. The Australian Standard differs from its British prototype by requiring the application of two coats of the fire retardant coating without primer, whereas the British Defence Standard requires a zinc chromate primer (the absence of primer in the Australian Standard raises questions about the relevance of the scheme to the system actually used by the Navy). Both methods require examination of the coating to see if flaming and blistering occur following the application of a flame to the reverse side of the panel. As such, both are unsuitable for intumescent paint evaluation.

The US Navy (40, 117) has developed a more severe test than AS K179-1969 to determine whether a paint will ignite into flames when the sole ignition source is the heated metallic substrate to which the paint adheres. The test is occasionally referred to as the 'Resistance to Ignition Test' and is modified from one described by Birnbaum & Markowitz (119). The apparatus consists of a high amperage direct current generator and ancilliary equipment to shunt the current directly through the test specimen to cause rapid heating. It is calibrated to give a temperature rise from within the test specimen of 1000°C within 60 seconds. Good fire retardant paints show little or no ignition whereas unretarded flammable paints frequently showed violent ignition characteristics followed by continued flaming.

In 1954 Lasch and Jukkola (2) surveyed the US Specifications for fire retardant coatings suitable for aircraft and considered them inadequate for coatings on metal surfaces. These workers therefore developed a procedure judged by backface temperature. Since that time, a number of specifications have appeared for determining backface temperatures as a measure of heat and fire resistance of coatings. The Royal Australian Air Force (RAAF) favours one of these procedures, the Lockhead Aircraft Corporation Specification No 37-676 'Coating Fire and Heat Resistant (118).' In this test, 12-15 mil thick coatings are required to maintain the backside of an 8 inch square coated aluminium panel below 550°F above ambient for 15 minutes when the coating is exposed to a 1000°F heat source. The coating must also not burn or blister when exposed to a 2000°F flame for 15 minutes. The flame must be generated using a natural gas-oxygen mixture suitably adjusted to cover a 5-inch diameter area. The panel must not be burned or blistered, but partial annealing is permissible.

Other tests for fire retardant paints include the ASTM D 1361 (stick and wick), the NASA T-3 JP-4 fuel-fired furnace test (51) and the quarter-scale compartment test (120). The first test is relatively old and not generally employed for intumescent or high performance coatings while the two latter tests have been restricted to specialist establishments. Individual researchers have designed a number of simple tests for fire retardant coatings including a propane torch method (91) which, it is claimed, creates a large thermal shock and determines if stable char formation can occur. Other workers (9) have discarded the propane torch claiming that the temperature (1200°C) was too high and that more characteristic results were obtained from flat flame burners which gave a range of reproducible flame temperatures.

9. SMOKE GENERATION AND TOXICITY

In the absence of a nonflammable, non-smoke producing, fire retardant coating, a variety of coatings have been developed. The limitations of combustible organic materials have given rise to a widespread attitude that while fire retardant coatings may be very effective in protecting substrates against combustion, these coatings increase smoke propagation thereby creating a problem greater than that of substrate combustibility. Very little is known about the factors controlling smoke generation during a fire. However, the addition of heavy metals has been found to be effective in suppressing smoke from PVC (121, 122).

Todd (34) reported that conventional chlorosulphonated polyethylene sheathings are flame retardant and have high oxygen index values but that in a fire they emit large volumes of smoke and high levels of hydrochloric acid gas. He found that the introduction of alumina trihydrate filler resulted in major reductions in smoke emission and the acid gas was restricted to less than 5% (a 50% reduction) at 800°C. American reports suggest that a paint coating has been developed for this cabling which meets US military requirements (123).

ICI Mond Division (124) report an 80% reduction in smoke generation from coated polyurethane foam by the introduction of either an alkyl phenyl phosphate or calcium zinc molybdate in a vinyl chloride/vinylidene chloride resin.

Toxicity evaluation is a field for which standard ISO methods have not been agreed. This remains an extremely important area for future progress in the field of fire retardancy.

10. CONCLUSIONS

This report reviews the various kinds of fire retardant coatings that have been used by the Services as well as those that have been reported in the literature and discusses theories on their mechanisms of action.

The field of fire retardant coatings is a complex one, complicating factors including different substrates, different requirements and different tests. At this time, no ideal coating is available which provides long term surface protection with excellent fire retardancy, negligible smoke and toxic vapor production for use on all substrates. Consequently, different fire retardant coatings are utilised depending on the application. However, the use of different coatings for similar applications is apparent among allied Services. This is believed to reflect the limited interaction between relevant personnel in the coatings field.

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11. REFERENCES

1. Yockers, J.R. (1953). *Effectiveness of Fire-Retardant Paints in Fire Prevention.* Adv. in Chem. Series 9. Symp. Fire Retardant Paints. ACS Los Angeles, 21-27.

2. Lasch, H.W. & Jukkola, E.E. (1953). Fire-Retardant Coatings for Aircraft Use. Adv. in Chem. Series 9. Symp. Fire Retardant Paints. ACS Los Angeles 67-81.

3. Vandersall, H.L. (1971). Intumescent Coating Systems, Their Development and Chemistry. J. Fire & Flammability. (2), April 97.

4. Chang, W.H., Scriven, R.L. & Blair Ross, R. (1975). *Flame-Retardant Organic Coatings.* in Flame Retardant Organic Materials. (eds Lewin, M., Atlas, S.M. & Pearce, E.M. Vol 1, p. 399. Plenum Press, New York.

5. Ryles, A.P. (1973). Intumescent Flame Retardant Paints; Their Formulation and Use. Paint Manufacture, September, 37.

6. Bishop, D.M, Bottomley, D & Zobel, F.G.R. (1948). Fire Retardant Paints. JOCCA (12), 373.

7. Jones, G. (1948). US Pat. 2,452,054.

8. Jones, G. (1948). US Pat. 2,452,055.

9. Ellard, J.A. (1973). Performance of Intumescent Fire Barriers. Am. Chem. Soc., Div. Org. Coat. Plast. Chem. Papers, 33, 1, 531.

10. Ablation and Ablative Materials, Vol 1, 1971-76. Published Search, NTIS/PS-78/0312.

11. Ablation and Ablative Materials, Vol 2. Published Search NTIS/PS-79 0381.

12. Wilson, E.L. (1978). Flammability and High-Temperature Characteristics of Composites. In Flame Retardancy of Polymeric Materials, Vol 3 (eds W.C. Karyla and A.J. Papa) Chapt. 4, 245.

13. Harris, L.A. (1986). Composites in Space – Past, Present and Future. Composite Interfaces. eds Ishida, H. and Koenig, J.L. Elsevier Co., Inc.

14. Walton, T.R. (1967). *The Influence of a Fire-retardant Undercoat on the Burning Characteristics of a Combustible Topcoat.* NRL Report 6548, Naval Research Laboratories, Washington.

15. Westgate, M.W. (1954). Fire Retardant Paints, Adv. in Chem, Series No 9, ACS. Los Angeles.

16. Van Krevelen, D.W. (1975). Some Basic Aspects of Flame Retardant Polymeric Materials, Polymer, 16, 615.

17. Aseeva, R.M. & Zaikov, G.E. (1985). Flammability of Polymeric Materials. Advanced Polymer Science 70, Key Polymers, Properties and Performance, p 172.

18. Conklin, M.N. (1922). The Fire-proofing or Flame-proofing of Textile Fabrics. Color Trade J., 11, 171.

19. Paimboeuf, L. (1837). US Pat. 449.

20. Felldin, L. (1884). US Pat. 291,176.

21. McCulloch, L. (1936). US Pat. 2,044,176.

22. Kalamaikowski, S. (1898). US Pat. 603,693.

23. Rigby Watson, J. (1933). US Pat. 1,900,211-2.

24. Jones, G. (1948). US Pat. 2,452,054.

25. Ware, R.P. & Westgate, M.W. (1948). Patent Survey of Fire-Resistant and Fire-retardant Compositions. National Paint, Varnish, Lacquer Assoc., Sci. Circ. No 727, 17-39.

26. Lyons, J.W. (1970). The Chemistry and Uses of Fire Retardants, Chapt. 6. Coatings, Wiley-Interscience.

27. Hindersinn, R.R. & Witschard, G. (1978). The Importance of Intumescence and Char in Polymer Fire Retardance. In Flame Retardancy of Polymeric Materials. (eds W.C. Kuryla & A.J. Papa) Marcel Dekker, N.Y. 4, 1.

28. Grubb, R. & Cranmer, W.W. (1954). Testing Fire-Retardant Paints under Simulated Service Conditions. In Fire Retardant Paints. Adv. in Chem. Series. 9. ACS. Los Angeles.

29. US Mil Spec. JAN-P-700. (1948).

30. McQuaide, P.B. (1980). The History and Goals of the Weapon Cook-Off Improvement Program. Pacific Missile Test Center, Point Mugu, California.

31. Anderson, C.E. Jr. & Wauters, D.K. (1984). A Thermodynamic Heat Transfer model for Intumescent Systems. Int. J. Engng Sci. 22, No 7. pp 881-9.

32. Pulley, D.F. (1978). Symp. Corrosion Control by Coatings. Lehigh University, Bethlehem, Penn.

33. Preston, A. (1982). Sea Combat off the Falklands. The Lessons that must be Learned. Willow Books.

34. Todd, D. (1982). Electric Cabling - Protection for Fire Risk Areas. Defence Communications and Security Review, No 82/3, pp 150-1.

35. Brown, D.K. (1984). Deputy Chief Naval Architect, 7th Inter-Naval Corrosion Conference, Canberra.

36. Furgeson, C. (1986). HM New Zealand Navy on secondment to MRL.

37. ABR 19/1978. RAN Painting Manual. Vol 2 Ships. Chapt. 4, Leaf 6.

38. Brown, J.R. & Dunn, P. (1976). Fire Hazards of Organic Materials - Small Scale Assessment of Flammability and Smoke Generation. Fire and Materials, 1, 2.

39. Pers. Comm. (1987). S. Rogers. NAVSEA Washington.

40. Gracik, T.D. & Morris, J.G. (1987). Correlation Between Thickness of Shipboard Paints and Small Scale Fire Tests. David W. Taylor Naval Ship Research and Development Center, Bethesda, Md. Ship Materials Engineering Dept.

41. Funt, J.M. & Magill, J.H. (1975). Estimation of the Fire Behaviour of Polymers. J. Fire Flammability, 6, (1), 28.

42. Lenz, R.W. (1967). Organic Chemistry of Synthetic High Polymers. Intersci. Publ., N.Y. 112.

43. Frazer, A.H. (1968). High Temperature Resistant Polymers. Intersci. Publ., N.Y.

44. Sharpe, M.H., Hill, W.E. & Simpson, W.G. (1978). Sprayable Low Density Ablator and application Process, US Pat. 4,077,921.

45. Fish, R., Parker, J. & Fohlen, G. (1976). Design, Synthesis and Development of New Transport Polymers for Military Applications, Air Force Materials Laboratory, Wright-Petterson AFB, Ohio Conference on Aerospace Transport and Enclosures, April.

46. Plastics Engineering Co. Sheboygan, Wisconsin, 1967. Advertising Brochures.

47. Currell, B.R. (1985). Inorganic Polymers in the Year 2000. Chemistry in Britain. June, pp 557-560.

48. Ray, N.H. Inorganic Polymers. London; Academic Press.

49. Ray, N.H. (1979). The Structure and Properties of Inorganic Polymer Phosphates. Br. Polymer J. 11, 163.

50. Harris, L.A. (1986). Composites in Space - Past, Present and Future. Composite Interfaces. eds Ishida, H. & Koenig, J.L. Elsevier Sci. Publ.

51. Anderson Jr., C.E., Dziuk Jr., J., Mallow, W.A. & Buckmaster, J. Intumescent Reaction Mechanisms, (1985), J. Fire Sci. 3, (3), 161.

52. Interam. 3M Co. St Paul, Minn. cited in Product Engineering, Feb. 1976. p 37.

53. Sawko, P.M. & Riccitiello, S.R. (1977). Intumescent Coatings Based on 4,4'-Dinitrosulfanilide, J. Coat. Tech. 49, No 624, 49.

54. Cook, J. (1987). TTCP-PTP-3 Note (Ref WAE/293/019) 'Intumescent Coatings - Possible Future Assignment' 22 July. MRL Registry File 64/4/12, Pt 2.

55. Parker, J.A., Fohlen, G.M., Sawko, P.M. and Griffin Jr., R.N. (1968). The Use of a Salt of p-Nitroaniline as a Component for Intumescent Coatings, SAMPE J. 4, 5.

56. Sawko, P.M & Riccitiello, S.R. (1977). Intumescent-Ablators as Improved Thermal Protection Materials, J. Coat. Tech. 49, No 627, 38.

57. Tech. Bull. 0667, Celanese Resins, Div. of Celanese Coatings Co., Louisville, Ky.

58. Porret, D. & Leumann, E. (1962). Epoxy Resins. VII. Fire Retardant Epoxy Resins. Chimia, 16, 72.

59. Clark,C.C. & Krawczyk, A.J. (1969). US Pat. 3,627,726.

60. Blair, N.D.,Witschard, G. & Hindersinn, R.R. (1972). Novel Fire Intumescent Coatings. J. Paint Tech., 44, (573), 75.

61. Barnstoff, H.D., Ames, D.P. & Chadwick, D.H. (1959). Paints, Plastics & Printing Ink Chemistry, 136th Meeting Am. Chem. Soc. p 178.

62. Saunders, J.H. & Frisch, K.C. (1961). Polyurethane Chemistry and Technology. Pt 1, Interscience, New York.

63. Waters, R.M. & Smith, J.C. (1968). US Pat. 3,372,208.

64. Skiff, R.A. (1963). US Pat. 3,073,799.

65. Chemische Werke Albert (1968). Belg. Pat. 715,110.

66. Brown, L.E. & Harshman Jr., J.B. AEC Accession No. 35935. Rept No. M-L-M.-CF-64-8-1.

67. Chen, H.H. & Nixon, A.C. (1965). Heat-Resistant Epoxy-Boroxine Foams for High Temperature Applications. SPE Trans. 5(2), 90.

68. Woods, W.G., English, W.D. & Bengelsdorf, I.S. (1966). US Pat. 3,257,347.

69. Martin, F.J. & Price, K.R. (1968). Flammability of Epoxy Resins, J. Appl. Polymer Sci., 12, 143.

70. Frisch, K.C. & Reegan, S.L. (1975). Relationship Between Chemical Structure and Flammability Resistance of Polyurethanes. in Flame Retardancy of Polymeric Materials. (W.C. Karyla & A.J. Papa eds) V. 3. p. 291. Marcel Dekker, New York.

71. Papa, A.J. (1975). Flame-Retarding Polyurethanes. In Flame Retardancy of Polymeric Materials. (W.C. Karyla & A.J. Papa eds) V. 3. p.1. Marcel Dekker, New York.

72. Schmidt, W.G. (1965). Flame-Retardant Additives in Plastic and Related Patents, Trans. J. Plastics Inst., 42, (5), 197 (1965).

73. Tilley, J.N., Nadeau, H.G., Reymore, H.E., Waszeciak, P.H. & Sayigh, A.A. (1968). Thermal Degradative Behaviour of Selected Urethane Foams Related to Variations of Constituents. II Chemical Reactions in Urethane Decomposition. J. Cell. Plast. 4, (2), 56.

74. Einhorn, I.N. & Mickelson, R.W. (1968). Char Formation in Rigid Urethane Foams. Div. Org. Coatings Plast. Chem., A.C.S. Preprints, 28 (1), 291.

75. Einhorn, E.I., Mickelson, R.W., Shah, B. & Craig, R. (1968). Smoke Development in Urethane Foams. J. Cell Plast. 4, 188.

24

76. Anderson, J.J. (1963). Retention of Flame Properties of Rigid Polyurethane
     Foams. Ind. Eng. Chem., Prod. Res. Dev. 2, 261.

77. Backus, J.K., Bernard, D.L., Darr, W.C. & Saunders, J.H. (1968).   J. Appl. Polym.
     Sci. 12, 1053.

78. Ball, G.W., Haggis, G.A., Hurd, R. & Wood, J.F. (1968).   New Heat Resistant
     Rigid Foam. J. Cell Plast. 4, 248, (1968).

79. Standard Oil Co. (1966). Neth. Appl. 6,604,906.

80. Hayash Jr., E.F., Reymore, H.E. & Sayigh, A.A. (1972).   US Pat. 3,673,128.

81. Karyla, W.C. (1973).   In Flame Retardancy of Polymeric Materials. (W.C. Kuryla
     & A.J. Papa, eds) V.1, p.1 Marcel Dekker, New York.

82. Backus, J.K., Darr, W.C., Gemeinhardt, P.G. & Saunders, J.H. (1965).   Thermal
     Decomposition of Rigid Urethane Foams. J. Cell. Plastics, 1, 178.

83. Parrish, D.B. & Pruitt, R.M. (1969).   Thermal Stability of Flame Resistant
     Flexible Urethane Foams, J. Cell Plastics, 5, 348.

84. Parker, J.A., Riccitiello, S.R., Gilwee, W.J. & Fisk, R. (1968).   Paper presented to
     the 25th Annual Conference of Society of Plastics Industries, San Francisco.

85. Hilado, C.J., Karyla, W.C., McLaughlin, R.W. & Proops, W.R. (1970).   Boron and
     Antimony Compounds as Fire Retardants in Rigid Polyurethane Foams, J. Cell
     Plast., 6, (5), 215.

86. Miles, C.E. & Lyons, J.W. (1967).   Properties of Rigid Urethane Foams Containing
     Fire Retardants Based on Phosphorus. J. Cell Plast., 3, 539.

87. Phos-chek P/30. Technical Bulletin IC/SCS-270, Monsanto Industrial Chemicals
     Co. St Louis, Mo.

88. Juda, W., Jones, G. & Altman, N. (1953).   US Pat. 2,628,946.

89. Piechota, H. (1965).   Some Relations Between raw Materials, Formulations and
     Flame Retardation of Rigid Polyurethane Foams. Kunststoff-Rundschau 12 (4),
     191.

90. Union Carbide Corp. West German Pat. 2,216,900 (1971).

91. Arapahoe Chemicals Technology Service Report No. 219U1, "TE55TM Smoke
     Suppressant with Polyurethane Foam for Low Smoke and Flame Retardancy".

92. Green, H.A. (1966). U.S. Pat. 3,262,894.

93. Myers, R.E., Dickens, E.D., Licursi, E & Evans, R.E. (1985).   Ammonium
     Pentaborate: An Intumescent Flame Retardant for Thermoplastic Polyurethanes.
     J. Fire Sci. 3, Nov/Dec 432.

94. Dyer, E. & Dunbar, R.A. (1970). Phosphorus-Containing Polymers. J. Polymer Sci.,
     Pt 1A - 8, 629.

95.   Hoye, P.A.T. & Coates, H. (1964) Brit. Pat. 974,033.

96.   Clark, C.C. & Krawczyk, A.J. (1968).   US Pat. 3,525,708.

97.   Kuehn, E. (1973).   US Pat. 3,728,138.

98.   Clark, C.C. & Krawczyk, A.J. (1968).   US Pat. 3,365,420.

99.   Pumpelly, C.T. & Larson, E.R. (1970).   US Pat. 3,542,740.

100.   Cordier, D.E. & D'Anciccio, V.V. (1971).   US Pat. 3,575,547.

101.   Konig, K., Muller, E. & Wagner, K. (1973).   US Pat. 3,723,392.

102.   Clark, C.C. & Krawczyk, A.J. (1969).   US Pat. 3,448,075.

103.   Carlson, R.D. & Hodan, J.J. (1970).   US Pat. 3,527,722.

104.   Krawczyk, A.J. (1971).   US Pat. 3,627,726.

105.   Burns, J.P., Feltzin, J. & Kuehn, E. (1972).   US Pat. 3,639,294.

106.   Melamud, S. & Feely, W.E. (1975).   Flame-Retardant Acrylic Polymers. Ch. 2 in
        Flame Retardancy of Polymeric Materials. Vol 3. (eds W.C. Kuryla & A.J. Papa).
        Marcel Dekker, N.Y.

107.   Owens-Corning Fiberglass Corp. (1966).   Product Testing Laboratories Report No.
        27456.

108.   Madorsky, S.L. (1964).   Thermal Degradation of Organic Polymers. Wiley-
        Interscience, N.Y. 315 pp.

109.   Gruntfest, I.J. & Young, E.M. (1962).   Actions of Flame proofing Additives on
        Poly(methyl methacrylate), Am. Chem. Soc. Div. Org. Coat Plast., Preprints. 21,
        (2), 113.

110.   Weil, E.D. (1978).   Phosphorus-Based Flame Retardants. in Flame-Retardant
        Polymeric Materials. 2, eds M. Lewin, S.M. Atlas & E.M. Pearce. p 126.

111.   J.L. O'brien. (1958).   W. Ger Pat. 1,100,287.

112.   Cass, R.A. & Raether, L.O. (1963).   Phosphorus Containing Esters for Flame
        Proofing Acrylic Resins. Am. Chem. Soc., Div. Org. Coating Plastics Chem.,
        Preprints 23, 82.

113.   Ship Material Committee. Sea Systems Controllate.   Annual Report 1985. Ref.
        D/SSC NA131/50/105/1.

114.   Parker, J.A. & Winkler, E.L. (1967).   The Effects of Molecular Structures. NASA
        TR R-276, Nov.

115.   Underwriters' Laboratories Inc., (1950).   Standard Test Method for Fire Hazard
        Classification of Building Materials.

116. Vandersall, H.L. (1967).   The Use of a Small Flame Tunnel for Evaluating Fire
      Hazard. J. Paint Technology, 39, (511) 494.

117. Military Specification DOD-C-24596 (SH) 6 November 1979. Coating Compounds,
      Nonflaming, Fire-Protective (Metric).

118. Lockheed Material Specification Coating - Fire and Heat Resistant. 37-676.
      October 26, 1960.

119. Birnbaum, L.S. & Markowitz. M. (1948).   Fire Retardant Paints. Ind. & Eng.
      Chem. March, 40, 400.

120. Sim, M.J.   Minute Paper N86/9256. 27 Apr 87.

121. L.C. Mitchell (1974).   US Pat. 3,821,151

122. L.C. Mitchell. (1974).   US Pat. 3,846,372.

123. Personal Comm. (1987).   S. Rogers NAVSEA Washington on PPG product
      'PITCHAR'.

124. ICI Report.   Vinyl Acrylic Polymers for Water Borne Coatings.
      GC/13039/14374/2ED/13/686.

TABLE 1

Coating Resin	Characteristics	Remarks
Polyurethane	Moderately flammable LOI 19.0	Easily flame retarded. Toxic gases a problem. Flame retarded with phosphates, halogens.
Epoxy polyamide	Moderately flammable LOI 19.8	Flame retarded with halogens phosphates, borates, alumina trihydrate.
Acrylics	Flammable LOI 17.3	Flame retarded with phosphates halogens, alumina trihydrate.
Alkyd	Flammable	Flame retarded with phosphates, halogens (chlorendic anhydride)
Vinylidene chloride	Nonflammable LOI 60.0	Used by US Navy

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AUTHOR(S)	CORPORATE AUTHOR
	Materials Research Laboratory
L.V. Wake	PO Box 50,
	Ascot Vale, Victoria 3032

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ABSTRACT

   A continued increase in the use of fire retardant coatings by the Australian
Defence Forces (ADF) is expected in view of the higher levels of composite and other
lightweight materials being employed in modern military equipment. However, the
increased smoke production reportedly associated with some fire retardant coatings has led
to differences of opinion on the relative benefits associated with their use. This aspect
combined with the growing awareness on health and safety factors associated with fire has,
in part, resulted in a variety of coatings and testing methods being adopted by allied Service
organizations. This review examines the field and discusses the mechanisms of action and
relative performance of fire retardant coatings in relation to the above. Coatings suitable
for use by the ADF are also discussed.

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